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## Using Alcohol Fuels in Dual Fuel Operation of Compression Ignition Engines: A Review

10 Fuels Lubricants & Fluid Technologies

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The Congress programme centres around the presentation of Technical papers on engine research and development, application engineering on the original equipment side and engine operation and maintenance on the end-user side. The topics of the 2016 event covered Product Development of gas and diesel engines, Fuel Injection, Turbochargers, Components & Tribology, Controls & Automation, Exhaust Gas Aftertreatment, Basic Research & Advanced Engineering, System Integration & Optimization, Fuels & Lubricants, as well as Users' Aspects for marine and land-based applications.

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## ABSTRACT

Because of global warming and increasing air pollution, alternative fuels are increasingly being considered for use in internal combustion engines (ICEs). Among the alternatives, alcohol fuels seem very interesting. They can be produced in a renewable way and possess certain advantageous properties that give them the potential to lower pollutants and CO<sub>2</sub> emissions from ICEs.

Methanol and ethanol are the most researched alcohols today. In fact, in some areas of the world, gasoline is blended with methanol or ethanol for use in spark ignition (SI) engines. These alcohols are ideally suited for SI engines because of their high octane number (low tendency to knock). That makes them, however, not very well suited for compression ignition (CI) engines which require high cetane number fuels. There exist, however, CI engine technologies that burn alcohol fuels. One of these technologies is Dual Fuel (DF) operation.

In DF operation, the engine runs effectively on two fuels. There exist several concepts to achieve this. One of these is to inject a mixture of diesel and alcohol fuel directly into the cylinder. Another is to separately inject diesel and alcohol fuel directly into the cylinder. A third concept (so-called fumigation) is to inject the alcohol fuel into the intake and the diesel directly into the cylinder (the homogeneous alcohol-air mixture is then ignited by a pilot injection of diesel). The paper will provide an overview of the literature regarding this fumigation concept.

This work has been carried out as a part of the LeanShips project. LeanShips stands for 'Low Energy And Near-to-zero emission Ships'. It is a Horizon 2020 (H2020) project funded by the European Commission aimed at developing green shipping technologies and bringing these to the market. One of the Work Packages of the LeanShips project, 'Demonstrating the Potential of Methanol as an Alternative Fuel' aims to demonstrate a high-speed heavy-duty marine diesel engine converted to Dual Fuel (DF) operation on methanol (and diesel) while achieving significant reductions of emitted pollutants.

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## INTRODUCTION

Because of global warming and increasing air pollution, alternative fuels are increasingly being considered for use in internal combustion engines (ICEs). Among the alternatives, alcohol fuels seem very interesting. They can be produced in a renewable way and possess certain advantageous properties that give them the potential to lower pollutants and CO<sub>2</sub> emissions from ICEs.

Methanol and ethanol are the most researched alcohols today. In fact, in some areas of the world, gasoline is blended with methanol or ethanol for use in spark ignition (SI) engines. These alcohols are ideally suited for SI engines because of their high octane number (low tendency to knock). That makes them, however, not very well suited for compression ignition (CI) engines which require high cetane number fuels. There exist, however, CI engine technologies that burn alcohol fuels. One of these technologies is Dual Fuel (DF) operation, in which the engine runs effectively on two fuels. There exist several concepts to achieve this [1-5]. One of the dual fuel concepts is to inject a mixture of diesel and alcohol fuel directly into the cylinder. Another is to separately inject diesel and alcohol fuel directly into the cylinder. A third concept (so-called fumigation) is to inject the alcohol fuel into the intake and the diesel directly into the cylinder (the homogeneous alcohol-air mixture is then ignited by a pilot injection of diesel).

Each concept comes with its own upsides and downsides. When injecting a mixture of diesel and alcohol fuel, the advantage is that only one injector is needed and the conversion to dual fuel operation is relatively straight forward. A big disadvantage is, however, that the substitution ratio cannot be changed instantaneously. Moreover, the substitution ratio is limited because diesel and alcohols do not mix well (this can be partly alleviated by emulsifying the mixture). When injecting the diesel and alcohol fuel separately into the cylinder, the substitution ratio can be changed instantaneously and more diesel can be substituted with alcohol fuel. The downside is that this concept requires two separate injectors (injecting directly into the cylinder) leading to a complex conversion. The fumigation concept is, on the other hand, easier to implement because the alcohol fuel is injected at lower pressure (compared to injecting it directly into the cylinder) and no cylinder head modifications are required. In addition, the engine intake is generally easily accessible. There are, however, sometimes knocking and/or ringing issues associated with this fumigation concept because of the premixed combustion of the alcohol fuel and the inherently high compression ratio of a diesel engine.

In the following sections, the performance and emissions of diesel engines converted to fumigation on alcohol fuel will be reviewed.

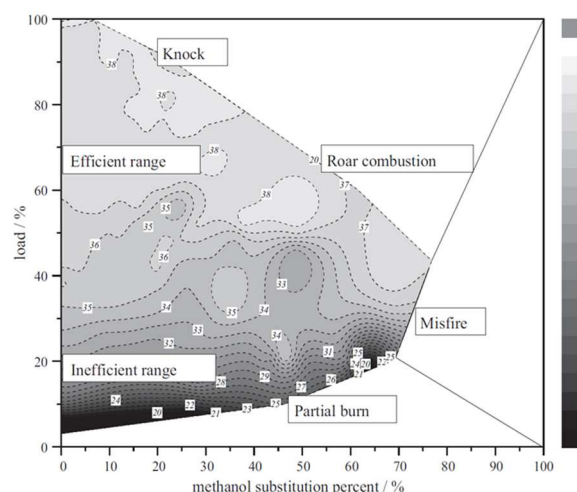
## SUBSTITUTION RATIO

The substitution ratio signifies how much of the diesel fuel consumption is replaced by alcohol fuel. It is defined as the percentage reduction of diesel fuel consumption in dual fuel mode (diesel and alcohol fuel) compared to diesel only mode [3, 4]:

$$s_a = \frac{\dot{m}_{d,D} - \dot{m}_{d,DF}}{\dot{m}_{d,D}}$$

where  $s_a$  signifies the alcohol fuel substitution ratio,  $\dot{m}_{d,D}$  the mass flow rate of diesel fuel in diesel only mode and  $\dot{m}_{d,DF}$  the mass flow rate of diesel in dual fuel mode.

Both for low and high loads, there is generally a limit to the substitution ratio as depicted in Figure 1. For low loads, there is an upper limit to the substitution ratio because of partial burn and/or misfire when too much alcohol is introduced into the cylinder. Under these conditions, the in-cylinder temperature might be too low and/or there might be too much excess air in the cylinder (mixture below lower flammability limit). For high loads, there is usually also an upper limit to the substitution ratio. This is because of knocking and/or ringing concerns. At high loads when more and more diesel fuel is substituted for alcohol fuel, there is a higher degree of premixed combustion. This in combination with the inherently high compression ratio of a diesel engine can cause knock. If this is the case, the substitution ratio has to be lowered to protect the engine. Alternatively, the compression ratio of the engine can be lowered by replacing the pistons with lower compression ratio ones. But this will add to the conversion cost and might compromise the cold-starting capability of the engine.



**Figure 1:** Experimental operating range of a diesel engine in dual fuel mode [3]

Instead of the substitution ratio, some authors use the alcohol fuel fraction in the total fuel consumption,

either on a mass basis or an energy basis. The alcohol fuel mass fraction is defined as [6]:

$$\phi_a = \frac{\dot{m}_{a,DF}}{\dot{m}_{a,DF} + \dot{m}_{d,DF}}$$

where  $\dot{m}_{a,DF}$  is the mass flow rate of alcohol fuel in dual fuel mode and  $\dot{m}_{d,DF}$  is the mass flow rate of diesel fuel in dual fuel mode.

The alcohol fuel energy fraction is defined as [7]:

$$\phi_a = \frac{\dot{m}_{a,DF} * LHV_a}{\dot{m}_{a,DF} * LHV_a + \dot{m}_{d,DF} * LHV_d}$$

Where  $\dot{m}_{a,DF}$  is the mass flow rate of alcohol fuel in dual fuel mode,  $\dot{m}_{d,DF}$  is the mass flow rate of diesel fuel in dual fuel mode and  $LHV_a$  and  $LHV_d$  are the Lower Heating Values of the alcohol fuel and diesel fuel respectively.

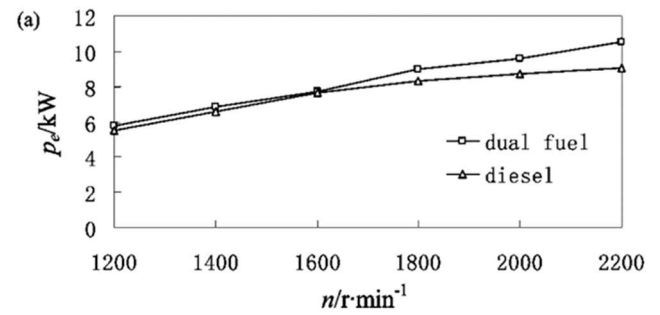
Of these two parameters, the most suited one is arguably the alcohol fuel fraction on an energy basis, because alcohol fuels (and especially alcohol fuels with only a few carbon atoms) have a lower energy content than diesel fuel.

## LOAD

As already mentioned in the previous paragraph, there is often a maximum to the substitution ratio at low loads due to too low temperatures and/or too much excess air. In the same way, there is a minimum load below which dual fuel operation is impossible. This can also be seen in Figure 1.

The maximum load of the engine is generally not or slightly negatively affected by fumigation [8]. However, in some cases an increase of the maximum load of the engine is reported (when knocking or ringing are not a concern). Such a result was obtained by Song et al. [6] who converted a Direct Injection (DI) single-cylinder diesel engine of 11 kW to dual fuel operation on methanol (fumigation). They conducted full-load experiments at various engine speeds and found a higher maximum load in dual fuel mode from 1800 rpm on. This can be seen in Figure 2.

Regarding cycle-by-cycle variations, Wang et al. [9] showed that dual fuel combustion is more stable at high loads than at low loads. At low loads, the Coefficients Of Variation (COVs) of the maximum temperature and pressure increased significantly when the substitution ratio was increased while at high loads the increases were only small. They also showed that in dual fuel operation Indicated Mean Effective Pressure (IMEP) fluctuated more at low loads than at high loads.



**Figure 2:** Full load engine power output at various engine speeds [6]

## EFFICIENCY

Efficiency is defined as [3]:

$$BTE = \frac{P_b}{\dot{m}_{d,DF} * LHV_d + \dot{m}_{a,DF} * LHV_a} * 100\%$$

where  $P_b$  is the brake power,  $\dot{m}_{d,DF}$  and  $\dot{m}_{a,DF}$  are the mass flow rates of diesel and alcohol fuel respectively, and  $LHV_d$  and  $LHV_a$  are the Lower Heating Values of diesel and alcohol fuel respectively.

Han et al. [5] reconfigured a four-cylinder production Ford diesel engine to a single-cylinder test engine which was converted to dual fuel operation on ethanol. The engine features a common-rail injection system (1600 bar) and has a compression ratio of 18.2:1. In their tests, they concluded that an increasing use of ethanol (up to 80%) slightly penalized the engine efficiency. However, in dual fuel mode the engine still managed to attain an efficiency between 41 and 46%.

Tutak et al. [10] studied alcohol (methanol and E85) fumigation on a three-cylinder naturally aspirated diesel engine with a compression ratio of 19:1. They conducted experiments at a fixed engine speed of 1500 rpm and at loads of 34%, 67% and 100% of the full load. In all the part load experiments, the brake thermal efficiency decreased with the increase of methanol or E85 fumigation. In the full load experiments, they observed a small increase in brake thermal efficiency from a methanol substitution ratio (based on energy fraction) of 75% on and from an E85 substitution ratio of 50% on. They attributed the lower brake thermal efficiency with alcohol fumigation at part loads to retarded combustion (longer ignition delay) and hence limited time for burning all the fuel (worse combustion efficiency). The higher brake thermal efficiency at full load for high alcohol substitution ratios was ascribed to a faster combustion (closer to constant volume combustion).

Cheng et al. [11] studied dual fuel operation with blended and fumigated methanol on a four-cylinder naturally aspirated diesel engine operating at a fixed speed of 1800 rpm, at five different loads. The

baseline operation on diesel was compared to operation on biodiesel, dual fuel operation on blended methanol (90% biodiesel and 10% methanol) and dual fuel operation on fumigated methanol (90% biodiesel and 10% methanol). Biodiesel operation outperformed baseline diesel operation at all loads. Dual fuel operation on blended methanol gave the best efficiency at low loads and dual fuel operation on fumigated methanol gave the best efficiency at medium and high loads. When comparing the biodiesel operation to the dual fuel operation on fumigated methanol, they concluded that at low loads the dual fuel operation performed worse and at medium and high loads performed better. The lower brake thermal efficiency at low loads was put down to a deterioration in combustion efficiency (too lean mixture). The higher brake thermal efficiency at medium and high loads was accredited to a better combustion (higher degree of premixed burning).

Song et al. [6] conducted methanol dual fuel experiments on a single-cylinder diesel engine with a compression ratio of 18:1. In their tests, they looked at equivalent brake specific fuel consumption  $BSFC_{eq}$  in which methanol consumption is converted to an equivalent diesel consumption according to the Lower Heating Value of methanol. This is analogous to studying the brake thermal efficiency as the brake specific fuel consumption is inversely proportional to the brake thermal efficiency. At both 1600 rpm and 2000 rpm, they observed higher  $BSFC_{eq}$  (lower BTE) at low loads for dual operation compared to normal diesel operation. They also found that the  $BSFC_{eq}$  increased (BTE decreased) with methanol mass fraction. They attributed this dual fuel behavior to a heat release being far away from top dead center due to lower burning velocity (leaner and colder mixture) and a postponed diesel ignition. At high loads, however, the  $BSFC_{eq}$  decreased (BTE increased) in dual fuel operation. This improvement became more pronounced with higher methanol mass fractions. This was ascribed to a faster combustion rate due to the higher flame speed of methanol.

Liu et al. [12] converted a single-cylinder diesel engine to dual fuel operation on methanol. They also observed a lower efficiency with increasing methanol fumigation at low loads and a higher efficiency with increasing methanol fumigation at high loads. In addition to the reasons already mentioned, they add an improved volumetric efficiency due to the evaporative cooling effect of fumigated methanol at high loads (high temperatures).

To summarize, with the fumigation method, sometimes a drop in efficiency occurs across the load range that gets more pronounced as the substitution ratio is increased. But in most cases, a slight decrease in efficiency is observed at low loads and a slight increase at high loads. In general, a lower efficiency can be attributed to a lower combustion efficiency and

a higher efficiency to a faster combustion (closer to the thermodynamically ideal isochoric combustion).

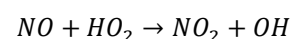
## EMISSIONS

**NO<sub>x</sub> EMISSIONS** - NO<sub>x</sub> emissions depend on three factors: in-cylinder temperature, residence time and availability of oxygen. The higher the in-cylinder temperature, the longer the high temperature combustion phase and the more oxygen is present in the cylinder, the more NO<sub>x</sub> will be produced. Of the three factors, the high temperature condition is the dominant one, i.e. the amount of NO<sub>x</sub> produced in an internal combustion engine depends mostly on temperature (cfr thermal NO<sub>x</sub>). NO<sub>x</sub> consists of NO and NO<sub>2</sub>.

Britto et al. [13] conducted dual fuel experiments with hydrated ethanol on a single-cylinder research engine with a compression ratio of 17:1. They report a reduction of the NO<sub>x</sub> emissions across the load range when applying ethanol fumigation. This reduction is attributed to the maximum temperature reduction in the combustion chamber by ethanol vaporization. This is evidenced by lower exhaust temperatures.

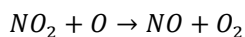
Jie Liu et al. [12] also report lower NO<sub>x</sub> emissions in dual fuel mode and the reductions are greater as more methanol is fumigated. They do not explicitly mention the cooling effect of methanol, but point to lower temperatures and a shorter residence time due to a prolonged ignition delay as being responsible for the reductions in NO<sub>x</sub> emissions.

Junheng Liu et al. [4] converted a six-cylinder turbocharged intercooled heavy duty diesel engine to dual fuel operation on methanol. Their results show lower NO<sub>x</sub> emissions, but higher NO<sub>2</sub> emissions in dual fuel mode (substitution ratio around 45%) compared to pure diesel mode. They report a reduction in NO<sub>x</sub> emissions of 42.3% at 30% load and of 23.1% at 80% load. But the NO<sub>2</sub> emissions in dual fuel mode are four times greater than those in diesel mode. They put the reductions in NO<sub>x</sub> emissions down to the cooling effect of methanol, lowering intake and combustion temperatures, and the faster combustion rate and hence reduced duration of high in-cylinder temperatures in dual fuel mode. They also mention the counteracting influence of the greater availability of oxygen due to methanol fumigation. The increased NO<sub>2</sub> emissions are attributed to an increased conversion of NO to NO<sub>2</sub> due to a higher availability of HO<sub>2</sub> radicals and a reduced conversion of NO<sub>2</sub> to NO. The conversion of NO to NO<sub>2</sub> occurs mainly through the following route [14]:



The conversion of NO<sub>2</sub> to NO happens through the following reaction [14]:





In dual fuel mode, generally, there remains some unburned methanol in the exhaust. They suspect that this unburned methanol acts as a source of HO<sub>2</sub> radicals which leads to an increased conversion of NO to NO<sub>2</sub>. Furthermore, the conversion of NO<sub>2</sub> back to NO is restrained because the cooling effect of methanol leads to more low-temperature regions in the cylinder. So, the interesting conclusion from their work is that in dual fuel mode NO emissions decrease and NO<sub>2</sub> emissions increase, but the overall NO<sub>x</sub> emissions are reduced. To quantify, at 30% load, the NO/NO<sub>x</sub> ratio is around 0.91 in diesel mode and around 0.25 in dual fuel mode.

Cheung et al. [15] performed dual fuel experiments with methanol on a four-cylinder naturally aspirated diesel engine with a compression ratio of 19:1 at various speeds and loads. They record lower NO<sub>x</sub> emissions at all speeds and loads. The higher the methanol substitution ratio, the greater the reduction. They point to two counteracting factors affecting NO<sub>x</sub> formation. On the one hand, with increasing methanol fumigation, more fuel bound oxygen is introduced into the cylinder. This might increase NO<sub>x</sub> formation. On the other hand, the cooling effect of methanol might reduce the temperature in the cylinder and hence reduce NO<sub>x</sub> formation. The reduction in NO<sub>x</sub> emissions (varying from 5.6% to 27.5% depending on speed and substitution ratio) points to the cooling effect of methanol as having the most influence. They also examined NO<sub>2</sub> emissions from the engine. Interestingly, this portion of the NO<sub>x</sub> emissions is higher in dual fuel mode compared to diesel operation and it increases with the methanol substitution ratio. The increase of NO<sub>2</sub> emissions is quite significant, varying from 2.9 to 5.7 times depending on speed and substitution ratio. They cite the oxidation of methanol, which acts as a source of HO<sub>2</sub> free radicals, in NO as a possible origin of NO<sub>2</sub>.

Wei et al. [16] converted a six-cylinder turbocharged intercooled diesel engine to dual fuel operation on fumigated methanol. Experiments were conducted at three loads (3.5, 6.2 and 8.8 bar Brake Mean Effective Pressure (BMEP)) and two speeds (1000 and 2000 rpm). They report lower NO<sub>x</sub> emissions in dual fuel mode compared to baseline diesel operation. The NO<sub>x</sub> emissions decreased with increasing substitution ratio. The reductions in NO<sub>x</sub> emissions ranged from 7.1% to 27.3% (depending on load and speed) at the maximum substitution ratio (up to 75%). They also report higher NO<sub>2</sub> emissions in dual fuel mode, rising as the substitution ratio is increased and an increased NO<sub>2</sub>/NO<sub>x</sub> ratio as more methanol is fumigated. They put forward several mechanisms through which these observations are explained. First, less NO is formed due to the lower in-cylinder temperature and reduced duration of high in-cylinder temperatures. The high latent heat of vaporization of methanol provides a

lower in-cylinder temperature at the compression stroke and the longer ignition delay and larger amount of premixed combustion reduce the local combustion temperature (less locally rich regions). In addition, the duration of high in-cylinder temperatures is reduced because of the premixed burning of methanol. Secondly, because the HO<sub>2</sub> radical is readily formed during the oxidation of methanol, lots of NO is converted to NO<sub>2</sub> through NO + HO<sub>2</sub> → NO<sub>2</sub> + OH. Because NO<sub>2</sub> is converted from NO and there is less NO to begin with, there is a decrease in NO<sub>x</sub> emissions. An interesting second part of their research was to add a Diesel Oxidation Catalyst (DOC) and study how this affected the emissions. They observed a slight increase in NO<sub>x</sub> emissions and a significant decrease in NO<sub>2</sub>/NO<sub>x</sub> ratio in dual fuel mode with the DOC. The chemical equilibrium reactions of NO and NO<sub>2</sub> in the DOC depend greatly on the amount of reductants. Very important in this respect are the increased amounts of CO and unburned hydrocarbons (HC) that are generally encountered in dual fuel fumigation operation. These reductants can reduce NO<sub>2</sub> to NO and can inhibit the oxidation of NO to NO<sub>2</sub> in the DOC. This explains the significant decrease of NO<sub>2</sub>/NO<sub>x</sub> ratio, but no interpretation is provided for the increase in NO<sub>x</sub> emissions.

Yao et al. [17] performed dual fuel experiments with methanol on a four-cylinder naturally aspirated diesel engine with and without an oxidation catalytic converter. They recorded lower NO<sub>x</sub> emissions at every load and speed in the dual fuel mode without oxidation catalyst compared to diesel operation. The maximum reduction was over 50%. They put this down to the cooling effect of methanol providing lower flame temperatures. In the dual fuel experiments with oxidation catalyst, slightly higher NO<sub>x</sub> emissions were observed compared to the dual fuel experiments without oxidation catalyst, but these were still lower than in the baseline diesel operation. They ascribe this to unburned HC and CO reacting in the oxidation catalyst with nitrogen in the presence of oxygen to form NO<sub>x</sub>.

Surawski et al. [18] converted a four-cylinder Ford diesel engine to dual fuel operation on ethanol. They set out to investigate the influence of vaporized ethanol on gaseous and particle emissions. So, as opposed to most other conversions, the fumigation system (with heat exchanger for vaporizing the ethanol) delivered vaporized ethanol to the intake manifold of the engine. Crucial to interpreting their results, is that this takes the cooling effect of ethanol out of the equation. They conducted their tests at 1700 rpm, at four load points and with ethanol energy fractions up to 40%. Reductions in NO emissions ranging from 20% at idle to 70% at half load are reported. They ascribe the substantial reduction in NO emissions to a lower excess air factor due to ethanol fumigation (ethanol is an oxygenate, but the vaporized ethanol displaces part of the intake air). This makes

the combustion more fuel rich and, hence, there is less oxygen and nitrogen available to form NO.

It can be concluded that a general drop in NO<sub>x</sub> emissions is observed across the load and speed range with the fumigation method. This reduction gets more pronounced as the substitution ratio is increased. The main reason for this is the cooling effect of the methanol that is fumigated in the intake of the engine. It provides lower in-cylinder temperatures greatly reducing thermal NO formation. The faster premixed combustion of methanol also shortens the combustion duration limiting the duration of high in-cylinder temperatures. This means there is less time for NO to be formed. Some authors also looked at NO<sub>2</sub> emissions and their relative share in the NO<sub>x</sub> emissions. It can be concluded that NO<sub>2</sub> emissions generally increase in fumigation operation and that their increase is proportional to the substitution ratio. The increase in NO<sub>2</sub> emissions is a result of the increased conversion of NO to NO<sub>2</sub> due to a higher availability of HO<sub>2</sub> radicals according to  $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ . The increased availability of HO<sub>2</sub> radicals comes from the oxidation of methanol during which the HO<sub>2</sub> radical is readily formed. Because of this, the NO<sub>2</sub>/NO<sub>x</sub> ratio is also increased in dual fuel mode. As NO<sub>2</sub> originates from NO and there is less NO to begin with, NO<sub>x</sub> emissions are decreased in fumigation operation.

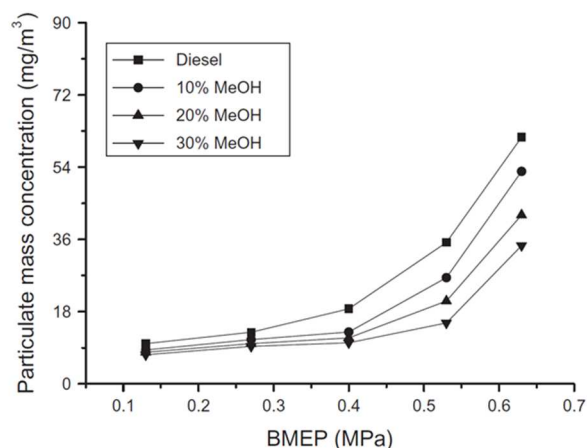
**PARTICULATE MATTER EMISSIONS** - Diesel particulate matter (PM) consists of carbonaceous soot, soluble organic fraction (SOF) and sulfates [2, 15, 19]. Diesel combustion has a high tendency to form soot. In a diesel engine, diesel is injected directly into the cylinder after the inlet valve has closed. Hence, there is little time to mix the diesel with air and consequently, locally rich zones exist at the time of combustion (high degree of diffusion burning). The composition and nature of the diesel fuel also contribute to the higher tendency to form soot. Diesel fuel consists of a blend of complex, heavy molecules (long chains and aromatics) with a lot of carbon-carbon bonds increasing the tendency for pyrolysis to form soot precursors.

Cheung et al. [15] modified an Isuzu four-cylinder, naturally aspirated diesel engine for dual fuel operation on methanol. Levels of methanol fumigation were 10, 20 and 30% (based on energy substitution). Engine tests were performed at several speeds (1280, 1920 and 2560 rpm) and loads (20, 40, 60, 80 and 95% of maximum engine load). They report a decrease of particulate mass concentration with an increase in the level of methanol fumigation. At the highest speed and with a substitution ratio of 30%, the particulate mass concentration could be reduced by up to 48%. This is ascribed to the fact that, with methanol fumigation, less diesel fuel is combusted in a methanol-air mixture. This leads to lower soot formation and hence also lower particulate matter formation. They also mention

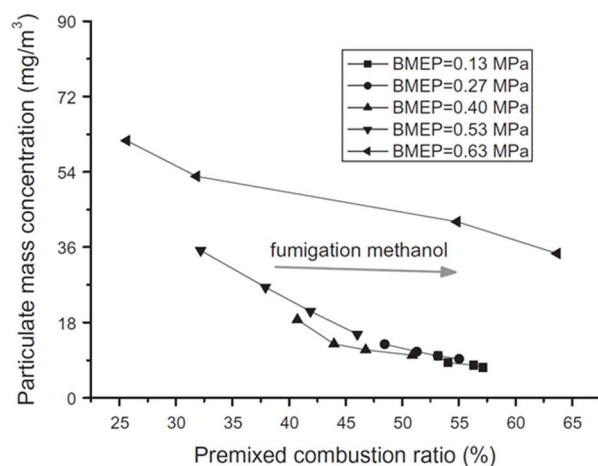
the sulfur and aromatic free nature and lower C/H mass ratio (compared to diesel) of methanol as contributing to the lower particulate mass concentration. But, interestingly, they also point to the potential of methanol fumigation to increase the soluble organic fraction of the PM via condensation of unburned hydrocarbons in the exhaust. They conclude, however, that the increase of SOF is outweighed by the decrease of soot and sulfates leading to a net reduction of the particulate mass concentration.

Zhang et al. [19] converted a four-cylinder, naturally aspirated Isuzu diesel engine to dual fuel operation. Tests were conducted at an engine speed of 1920 rpm and 5 different loads (0.13, 0.27, 0.40, 0.53 and 0.63 MPa). The energy contribution of the fumigated methanol was varied from 0 to 30%. They recorded lower particulate mass concentrations in dual fuel mode compared to pure diesel mode. The reductions in particulate matter were greater at higher loads and higher fumigation levels as can be seen in Figure 3. The reduction in PM is down to two reasons according to the authors. First, less diesel fuel is combusted because part of the energy comes from the combustion of methanol. Consequently, less diesel fuel is burned in the diffusion mode leading to a reduced formation of soot. Secondly, the longer ignition delay (caused by the cooling effect of methanol) provides more time for the diesel spray to break up, evaporate and mix with air. Consequently, more diesel fuel will burn in the premixed mode. This again reduces the amount of diesel fuel that is burned in the diffusion mode further reducing the formation of soot. As the formation of soot is reduced, so is the formation of PM. As the authors point out, it is interesting to investigate the relation between particulate matter and the degree of premixed burning. They therefore define the premixed combustion ratio as the ratio of the energy released in the premixed mode to the total energy supplied. The energy released in the premixed mode is evaluated from the heat release rate curve. Figure 4 shows the particulate mass concentration as a function of the premixed combustion ratio. For all loads it can be seen that an increase in the premixed combustion ratio leads to a lower particulate mass concentration. For the lowest loads, higher methanol fumigation levels only lead to a small increase of the premixed combustion ratio. Consequently, the particulate mass concentration only drops slightly. For the highest loads, however, higher methanol fumigation levels lead to a larger increase of the premixed combustion ratio with a corresponding larger reduction of the particulate mass concentration. Beside the particulate mass concentration, Zhang et al. also looked at the particle number concentration. They report a lower particle number concentration (compared to pure diesel operation) across all loads when fumigation methanol is applied and the reduction increases with the level of fumigation. The reduction was up to 57% for a fumigation level of 30% at 0.4

MPa BMEP. They also noted a decrease of the geometric mean diameter (GMD) of the particles with increasing fumigation level for the higher loads, while for the lower loads there was no significant change. They suspect that the smaller GMD is due to the increase of unburned hydrocarbons (with higher fumigation levels) which leads to more particulate nucleation during the dilution process when the unburned hydrocarbons are cooled.



**Figure 3:** Particulate mass concentration as a function of load (BMEP) [19]



**Figure 4:** Particulate mass concentration as a function of premixed combustion ratio [19]

Cheng et al. [11] also investigated the particle number concentration and size distribution on a four-cylinder, naturally aspirated diesel engine modified for dual fuel operation. With a methanol fumigation level of 10%, they did not see a significant change of the particle number concentration, but did record a shift towards smaller particles leading to a smaller geometric mean diameter. They suspect that this is due to the nucleation and condensation of unburned hydrocarbons associated with fumigating methanol.

Yao et al. [17] performed dual fuel experiments (methanol fumigation) on a modified four-cylinder,

naturally aspirated diesel engine. The test setup is equipped with an oxidation catalyst to investigate its effect on the emissions. They observed a reduction in smoke opacity (expressed in Bosch Smoke Units) in the dual fuel mode compared to pure diesel mode. The smoke could be reduced by up to 50%. They claim a smaller degree of diesel diffusion burning and methanol's low sooting tendency properties are the drivers behind this. Less diesel is combusted in the diffusion mode, because less diesel is injected into the combustion chamber and the diesel also has more time to evaporate and mix with air because of the longer ignition delay caused by methanol's cooling effect. The combustion of methanol does not tend to form soot, mainly because of its premixed nature but also because methanol is a simple molecule with a low molecular weight. It also contains a lot of oxygen, but no sulfur nor aromatics. In addition, the authors cite methanol's high flame speed as being beneficial to suppression of soot formation. With the oxidation catalyst, the maximum smoke reduction increased to around 80% which is ascribed to oxidation of the soot particles.

Geng et al. [2] also investigated the effect of an oxidation catalyst on the PM emissions of a dual fuel engine. They found that the oxidation catalyst was able to further reduce both the particulate mass and number concentrations in dual fuel mode. They put this down to oxidation of the unburned hydrocarbons and the soluble organic fraction of the particulate matter.

Liu et al. [4] converted a six-cylinder, turbocharged diesel engine with common rail injection system to dual fuel operation on methanol. The aim of their study was to assess the effect of the injection pressure of diesel on the performance and emissions of the engine in pure diesel and dual fuel mode. They observed lower smoke emissions in dual fuel mode (methanol fumigation) than in the baseline pure diesel mode. Beside the reasons cited by other authors, they also mention the OH radicals that are formed during the oxidation of methanol. These radicals can oxidize soot precursors thus lowering smoke emissions. They also noted that the smoke emissions in the dual fuel mode decreased with increasing diesel injection pressure. This is because the higher injection pressure provides a better atomization of the diesel spray. Hence, the diesel droplets will evaporate faster and mix more easily with the surrounding air. The result is more premixed and less diffusion burning of diesel fuel leading to reduced soot formation. The higher combustion temperature associated with the more homogeneous diesel-air mixture also provides for faster oxidation and more complete combustion.

For a detailed description of the chemico-physical features of the soot emitted by a dual fuel engine, the reader is referred to the paper [20] by Gargiulo et al.



To summarize the findings above, soot emissions are suppressed in dual fuel operation. This is because part of the diesel consumption is replaced by alcohol fuel which contains no aromatics, has fewer carbon-carbon bonds (methanol, in fact, has no carbon-carbon bonds) and is oxygenated. Alcohol fuels are also simple molecules with a low molecular weight. In addition, the alcohol fuel is premixed with air so there is a very low tendency to form locally rich zones. Moreover, because of the high heat of vaporization of alcohols, the ignition delay is usually increased giving the diesel more time to evaporate and mix with air. Consequently, fewer locally rich zones of diesel are formed (less diffusion burning) lowering soot emissions. The OH radicals that are formed during the oxidation of methanol also aid in oxidizing soot precursors.

The soluble organic fraction of the particulate matter emissions is generally increased. This relates to the increase of unburned hydrocarbon emissions that is usually encountered with dual fuel operation (see paragraph 'Hydrocarbon emissions').

The sulfates emitted by a diesel engine are suppressed in dual fuel operation, because alcohol fuels contain no sulfur.

Overall, the PM emissions (particulate mass concentration) generally decrease. There is, however, no agreement in literature on the particulate number concentration. Regarding the particle size distribution, a shift towards smaller particles is often observed because of nucleation and condensation of unburned hydrocarbons leading to a smaller geometric mean diameter.

**TRADE-OFF  $\text{NO}_x$ -PM** - Normally, in pure diesel operation a trade-off is observed between  $\text{NO}_x$  and particulate matter emissions. When the engine settings are modified to lower the  $\text{NO}_x$  emissions, the PM increases and vice versa.

Liu et al. [12] conducted dual fuel experiments on a single-cylinder diesel engine. They observed a simultaneous reduction in  $\text{NO}_x$  and smoke emissions under all loads as the methanol substitution ratio was increased. The 'breaking' of the traditional  $\text{NO}_x$ -smoke trade-off is attributed to methanol's high latent heat of evaporation, which leads to a lower initial temperature at the start of compression, the increased homogeneity of the mixture, which decreases local high temperatures, and methanol's oxygenated nature.

Song et al. [6] and Wei et al. [16] also recorded a simultaneous reduction in  $\text{NO}_x$  and smoke emissions with increasing methanol fumigation level.

It can be concluded that the trade-off relation between  $\text{NO}_x$  and PM emissions that is observed in pure diesel operation, disappears in dual fuel mode. In other

words, alcohol fumigation allows to simultaneously reduce both  $\text{NO}_x$  and PM emissions. The reasons why both these emissions decrease with increasing alcohol fumigation can be found in the relevant sections.

**CO EMISSIONS** - CO is an intermediate product of combustion. Its presence in exhaust gases signals incomplete combustion caused by low combustion temperatures or a lack of oxygen. In a conventional diesel engine, CO emissions are low because the engine operates with a high excess air factor meaning that there is more oxygen available for combustion than is stoichiometrically required.

Liu et al. [4] conducted dual fuel experiments with methanol on a modified six-cylinder, turbocharged engine. They found higher CO emissions compared to pure diesel operation. This is ascribed to a reduced CO oxidation rate caused by methanol's evaporative cooling effect.

Tutak et al. [10] investigated the effect of methanol and E85 fumigation on a three-cylinder, naturally aspirated diesel engine. They recorded higher CO emissions in fumigation mode compared to pure diesel operation with higher increases at partial loads than at full load. This is because lower loads correspond to lower temperatures which gets compounded by methanol and E85's cooling effect.

Surawski et al. [18] also found higher CO emissions with increasing fumigation level in dual fuel mode. They point to a decreasing excess air factor with increasing fumigation level leading to a richer combustion.

Yao et al. [17] investigated the emissions of a four-cylinder, naturally aspirated diesel engine modified for dual fuel operation on methanol. They also looked at the effect of an oxidation catalyst on the emissions. They recorded higher CO emissions in dual fuel mode compared to the baseline diesel operation, but the catalyst was able to reduce the CO emissions below those of the baseline diesel case. In this respect, Wei et al. [16] noted that in their dual fuel experiments at low load and speed, the exhaust temperature was below the light-off temperature of the catalyst (240-250°C) so that the catalytic efficiency was low. At this low load and speed in dual fuel mode, the catalyst was able to reduce CO emissions, but they were still well above the level of pure diesel operation. At higher loads and speeds, the exhaust temperature exceeded the catalyst's light off limit and CO emissions were similar to those in the baseline diesel case.

To summarize, CO emissions are higher in dual fuel mode than in pure diesel operation and they also increase with increasing fumigation level. This is due to the lower temperatures associated with the higher heat of vaporization of alcohol fuels. The lower

temperature impedes the full oxidation of the fuel. This increase is most pronounced at low loads.

**HYDROCARBON EMISSIONS** - Unburned hydrocarbon emissions are just as CO an indicator of the quality of the combustion. When high levels of unburned hydrocarbons are detected in the exhaust, it signals incomplete combustion. Higher HC emissions are typical of Port Fuel Injection (PFI) combustion such as in a petrol engine. In a conventional diesel engine HC emissions are normally low.

Cheung et al. [15] converted a four-cylinder, naturally aspirated Isuzu diesel engine to dual fuel operation on methanol. They recorded higher HC emissions in dual fuel mode compared to pure diesel operation. At all loads and speeds, the HC emissions increased with increasing substitution ratio. They also found that HC emissions decreased with increasing loads. The higher HC emissions in dual fuel mode are attributed to PFI effects and a lower combustion temperature. Because of the fumigation of methanol in the intake of the engine, some of the methanol-air mixture is quenched by the cold cylinder walls, absorbed by the oil film or trapped in crevices. This part of the methanol-air mixture escapes combustion and leads to higher HC emissions. This is aggravated by the lower combustion temperatures associated with methanol's cooling effect which impede oxidation of the fuel.

Similar observations and explanations are given by Cheng et al. [11], Yao et al. [17] and Tutak et al. [10]. As the fumigation level increases and more methanol is introduced into the cylinder, these effects get obviously progressively worse and further increasing HC emissions are the result. With higher loads, the HC emissions decrease due to a higher combustion temperature which facilitates oxidation of the fuel.

Beside the aforementioned reasons, Liu et al. [4] also point to the scavenging process as a potential source of HC emissions. When the inlet and exhaust valve are simultaneously open (valve overlap), some of the methanol-air mixture can escape the cylinder without combusting and lead to increased HC emissions. This can be a particular concern for turbocharged dual fuel engines.

Wei et al. [16] and Yao et al. [17] both showed that an oxidation catalyst in the exhaust can effectively reduce the HC emissions.

It can be concluded that unburned hydrocarbon emissions are higher in dual fuel mode than in pure diesel operation due to PFI effects and a lower combustion temperature, both associated with the fumigation of alcohol fuel. With a higher substitution ratio, more alcohol fuel is introduced into the cylinder and the HC emissions increase further.

**CO<sub>2</sub> EMISSIONS** - Cheng et al. [11] investigated the emissions of a diesel engine modified for dual fuel operation on methanol. Through fumigation of methanol the brake specific CO<sub>2</sub> emissions decreased by 2.5%. This is ascribed to the higher brake thermal efficiency in fumigation mode and methanol's lower carbon intensity (one unit of chemical energy contains less carbon).

Liu et al. [4] recorded lower CO<sub>2</sub> concentrations in dual fuel mode compared to pure diesel operation. Methanol's lower carbon intensity and the lower degree of fuel oxidation in dual fuel mode (less fuel is completely oxidized to CO<sub>2</sub> as evidenced by increased CO and HC emissions) are mentioned as the reasons behind this.

Cheung et al. [15] observed a mixed image regarding the CO<sub>2</sub> concentration. At low loads there is no significant change of CO<sub>2</sub> concentration when methanol is fumigated, but at high loads the concentration decreased with increasing fumigation level. Important in this respect is that in dual fuel mode, the thermal efficiency decreased at low loads, but increased at high loads. So at low loads, the increased fuel consumption (lower efficiency) is offset by the reduced degree of fuel oxidation and methanol's lower carbon intensity adding up to no real change in CO<sub>2</sub> concentration. At high loads, there is a lower fuel consumption (higher efficiency) and a decrease in CO<sub>2</sub> concentration is observed by up to 7.4%.

No general conclusion can be drawn on CO<sub>2</sub> emissions in dual fuel mode. It can, however, be said that methanol's lower carbon intensity and the reduced degree of fuel oxidation are beneficial for reducing CO<sub>2</sub> emissions. But ultimately, it is down to the efficiency whether or not CO<sub>2</sub> emissions are reduced. As discussed in the section about efficiency, no general conclusion can be drawn and hence, the same is true for CO<sub>2</sub> emissions.

## CONCLUSIONS

The following conclusions can be drawn from the literature regarding dual fuel operation on alcohol fuels:

- There is generally a limit to the substitution ratio, both at low loads (partial burn and/or misfire) and high loads (knocking and/or ringing).
- In most cases, the efficiency decreases slightly at low loads (lower combustion efficiency) and increases slightly at high loads (faster combustion) compared to pure diesel operation.
- Across all loads and speeds, there is a reduction of NO<sub>x</sub> emissions compared to pure diesel operation and the reduction is proportional to the substitution ratio. The main

reason for this is the cooling effect of the alcohol fuel that provides lower in-cylinder temperatures.

- In dual fuel operation, particulate matter emissions decrease compared to pure diesel operation. This is mainly due to the decrease of soot emissions because part of the diesel consumption is replaced with alcohol fuel that has a very low sooting tendency (premixed with air, simple molecule, oxygenated, fewer carbon-carbon bonds than diesel).
- In dual fuel operation, the traditional NO<sub>x</sub>-PM trade-off that is encountered in pure diesel operation is broken meaning that both NO<sub>x</sub> and PM emissions can be decreased.
- CO emissions in dual fuel operation are higher than in pure diesel operation because of lower temperatures due to the alcohol fuel's evaporative cooling effect.
- Unburned hydrocarbon emissions in dual fuel operation are higher than in pure diesel operation because of PFI effects (mixture quenched by walls, absorbed by oil, trapped in crevices) and lower temperatures, both related to the fumigation of the alcohol fuel.

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